

<H1>Additional Objective Questions

<H2> Single Correct Choice Type

1.(A) Equations of zero order are called zero order equations, for example, photochemical reaction between H_2 and Cl_2 .

2.(C) Rate at a particular instant of time.

3.(A) Using half-life period method,

For first order reaction, $k_1 = 0.693/t_{1/2} = 0.693/40$

For zero order reaction $k_0 = [A]_0/2t_{1/2} = 1.386/(2 \times 20)$

Therefore,

$$\frac{k_1}{k_0} = \frac{(0.693/40)}{(40/1.386)} = 0.5 \text{ mol}^{-1}$$

4.(A) According to the Arrhenius equation $k = Ae^{-E_a/RT}$. As temperature increases, rate constant (k) increases exponentially.

5.(D) $aG + bH \rightarrow$ Products. The rate is directly proportional to $[G]^m[H]^n$

When concentration of both the reactants is doubled then,

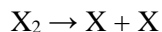
$$\text{Rate} = [2G]^m[2H]^n = 2^m 2^n [G][H]$$

Then the rate increases eight times which means either $m = 2$ then $n = 1$ or $n = 2$ and $m = 1$. Again, it is given that when the concentration of G is doubled then rate is doubled which means that $m = 1$ and $n = 2$. And the overall order is $m + n = 2 + 1 = 3$.

6.(C) The overall rate of the reaction depends on the rate of the slowest step. Since, two reagents are involved in the rate determining step; the overall rate of reaction is proportional to the concentrations of only those reagents.

$$\text{Rate} = k[X][Y_2] \quad (1)$$

From



$$k_{\text{eq}} = \frac{[X]^2}{[X_2]}$$

$$[X] = \sqrt{k_{\text{eq}} [X_2]}^{1/2} \quad (2)$$

From Eq. (1) and Eq. (2), we get

$$\begin{aligned} \text{Rate} &= k \sqrt{k_{\text{eq}}} [X_2]^{1/2} [Y_2] \\ &= k' [X_2]^{1/2} [Y_2] \end{aligned}$$

Thus, the overall order of the reaction = $1 + 0.5 = 1.5$

7.(A) For first order reactions, we have
$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A_t]} \quad (1)$$

Substituting the values in Eq. (1), we get

$$\begin{aligned}
 t &= \frac{2.303}{10^{-2}} \log\left(\frac{20}{5}\right) \\
 &= \frac{2.303}{10^{-2}} \times 0.60205 \\
 &= 138.6\text{s}
 \end{aligned}$$

8.(D) The decomposition reaction is $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$

Let $r_1 = 1 \text{ torr s}^{-1}$, when 5% reacted (95% unreacted)

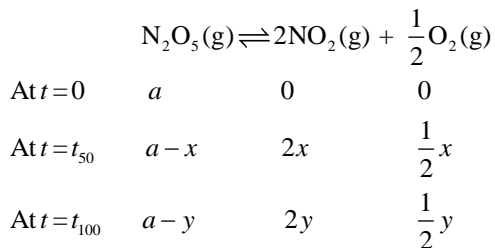
$r_2 = 0.5 \text{ torr s}^{-1}$, when 33% reacted (67% unreacted)

We know $r \propto (a - x)^m$

where a is the initial concentration, x is the amount reacted at time t and m is the order of reaction.

$$\begin{aligned}
 \frac{r_1}{r_2} &= \left(\frac{a - x_1}{a - x_2}\right)^m \\
 \frac{1}{0.5} &= \left(\frac{0.95}{0.67}\right)^m \\
 2 &= (1.41)^m \Rightarrow 2 = (\sqrt{2})^m \Rightarrow m = 2
 \end{aligned}$$

9.(D) The decomposition reaction is



Given, $a = 50 \text{ mm Hg}$

At $t = t_{50\text{min}}$

$$\begin{aligned}
 a - x + 2x + \frac{1}{2}x &= 87.5 \\
 a + \frac{3}{2}x &= 87.5 \\
 \frac{3}{2}x &= 87.5 - 50 = 37.5 \Rightarrow x = \frac{37.5 \times 2}{3} = 25
 \end{aligned}$$

For first order reaction

$$kt = 2.303 \log\left(\frac{a}{a - x}\right)$$

At 50 min

$$kt = 2.303 \log\left(\frac{50}{50 - 25}\right)$$

$$kt = 2.303 \log 2$$

$$k = \frac{2.303 \times 0.3010}{50}$$

At 100 min

$$kt = 2.303 \log \left(\frac{a}{a-y} \right)$$
$$100 \times \frac{2.303 \times 0.3010}{50} = 2.303 \log \left(\frac{50}{a-y} \right)$$
$$2 \times 0.3010 = \log \left(\frac{50}{a-y} \right)$$
$$\frac{50}{a-y} = 4$$
$$a-y = \frac{50}{4} = 12.5$$
$$50-y = 12.5 \Rightarrow y = 37.5$$

Therefore, total pressure at 100 min can be calculated as

$$\begin{aligned} \text{Total pressure} &= a - y + 2y + \frac{1}{2}y \\ &= a + \frac{3}{2}y \\ &= 50 + \frac{3}{2} \times 37.5 = 106.25 \text{ mm Hg} \end{aligned}$$

10.(C) As rate varies as $(1.5 X)^2$ so the order of the reaction is 2.

11.(B) Value of k is independent of the initial concentration of A and B. Rate constants are independent of concentration but depend on other factors, such as temperature.

12.(A) This is because the minimum number of reactants is two, so the molecularity cannot be one (for molecularity = 1, there should be only one reactant).

13.(B) According to first order reaction,

$$t_{1/4} = \left(\frac{2.303}{k} \right) \log \left(\frac{1}{1-1/4} \right) = \frac{0.29}{k}$$

14.(A) We know

$$\log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Or

$$E_a = 2.303R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \times \log \left(\frac{k_2}{k_1} \right) \quad (1)$$

Given, $k_2 = 2k_1$; $T_1 = 300 \text{ K}$; $T_2 = 310 \text{ K}$

Substituting the values in Eq. (1), we get

$$E_a = 2.303 \times 1.987 \left(\frac{300 \times 310}{310 - 300} \right) \times \log \left(\frac{2k_1}{k_1} \right)$$

$$\Rightarrow E_a = 2.303 \times 1.987 \left(\frac{300 \times 310}{10} \right) \times \log 2$$

$$E_a = 12.9 \text{ kcal mol}^{-1}$$

15.(A) This is in accordance with Arrhenius equation $k = Ae^{-E_a/RT}$

16.(B) From the given reaction, the concentration of B can be written as,

$$[B] = \frac{m}{n} [A]_0$$

17.(C) From the reactions, we have

The rate of disappearance of A is

$$-\frac{d[A]}{dt} = 2k_1[A]^2 \quad (1)$$

The rate of formation of A from the backward reaction is

$$-\frac{d[B]}{dt} = +\frac{1}{2} \frac{d[A]}{dt} = k_2[B] \quad (2)$$

$$\Rightarrow \frac{d[A]}{dt} = 2k_2[B]$$

Therefore, Eq (1) – Eq (2) gives the net rate of disappearance of A

$$= 2k_1[A]^2 - k_2[B]$$

18.(B) E_a is the activation energy which represents the minimum energy that the reacting molecules must possess before undergoing a reaction. As E_a increases, the rate constant k decreases.

19.(D) From the given reactions, the rate expressions for the second reaction is

$$\text{Rate} = k[\text{NOBr}_2][\text{NO}]$$

However, $[\text{NOBr}_2] = K_c[\text{NO}][\text{Br}_2]$. Therefore,

$$\text{Rate} = k \cdot K_c[\text{NO}][\text{Br}_2][\text{NO}] \text{ where } K_c = \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]}$$

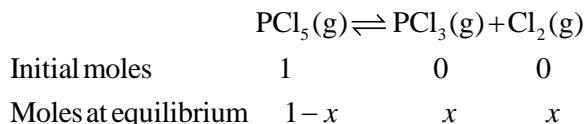
or
$$\text{Rate} = k[\text{NO}]^2[\text{Br}_2]$$

20.(D) Rate is determined by the slowest step. Therefore, the rate law for the given reaction is

$$\text{Rate} = k[\text{O}_3][\text{O}]$$

21.(D) This is based on Arrhenius equation which is given as $\log k = \log A - \frac{E_a}{2.303 RT}$

22.(A) The reaction can be represented as

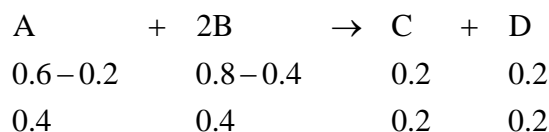


The total number of moles at equilibrium = $1-x+x+x = 1+x$

Hence, the partial pressure of PCl_3 is

$$p_{\text{PCl}_3} = \left(\frac{x}{x+1} \right) p$$

23.(D) $r_1 = k[\text{A}][\text{B}]^2 = k[0.6][0.80]^2$. The reaction involved is



Comparing the rates, we get

$$\frac{r_2}{r_1} = \frac{(0.4)(0.4)^2}{(0.6)(0.8)^2} = \frac{1}{6}$$

24.(B) In the reaction $2\text{A} + \text{B} \rightarrow \text{Products}$, when concentration of B is doubled, the half-life did not change, hence the reaction is of first order with respect to B because half-life is independent of concentration for first order reaction ($t_{1/2} = 0.693/k$). When concentration of A is doubled, the reaction rate is doubled, hence the reaction is of first order with respect to A. So, the overall order is $1 + 1 = 2$ and the units of rate constant for a second order reaction are $\text{L mol}^{-1} \text{s}^{-1}$.

25.(A) From the given rate, the order = $1 + 2 = 3$

26.(A) From the given reaction, the rate = $k[\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-]$.

27.(C) The half-life and rate constant relation for the first order reaction is

$$k = \frac{0.693}{t_{1/2}}$$

Therefore,
$$k = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}.$$

28.(B) In general, $k = [\text{conc.}]^{1-n} \text{ min}^{-1}$.

For third-order reaction = $[\text{molL}^{-1}]^{1-3} \text{ min}^{-1}$

$$= \text{L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

29.(A) Amount of A left in n_1 halves = $\left(\frac{1}{2} \right)^{n_1} [\text{A}]_0$

Amount of B left in n_2 halves = $\left(\frac{1}{2}\right)^{n_2} [B]_0$

At the end, according to the question

$$\frac{[A]_0}{2^{n_2}} = \frac{[B]_0}{2^{n_2}} \text{ or } \frac{4}{2^{n_1}} = \frac{1}{2^{n_2}}, [[A]_0 = 4[B]_0]$$

Therefore, $\frac{2^{n_1}}{2^{n_2}} = 4$ or $2^{n_1-n_2} = (2)^2 \Rightarrow n_1 - n_2 = 2$

Therefore, $n_2 = (n_1 - 2)$ (1)

Also $t = n_1 \times t_{1/2(A)}$; $t = n_2 \times t_{1/2(B)}$

(Let concentration of both become equal after time t)

Therefore, $\frac{n_1 \times t_{1/2(A)}}{n_2 \times t_{1/2(B)}} = 1$ or $\frac{n_1 \times 5}{n_2 \times 15} = 1$ or $\frac{n_1}{n_2} = 3$ (2)

For Eqs. (1) and (2), $n_1 = 3, n_2 = 1 \Rightarrow t = 3 \times 5 = 15 \text{ min}$.

30.(A) Comparing it with straight line equation $y = mx + c$, if we plot a graph between time vs. $\log C_t$, we get slope as R and intercept as $\log C_0$.

31.(B) The rate increases with temperature exponentially.

32.(D) We know

$$\frac{\text{Half life}}{\text{Initial pressure}} = \frac{290}{65} = 4.46 \text{ and } \frac{820}{185} = 4.43.$$

The values nearly agree. Therefore, the reaction is of zero-order.

$$\frac{x}{105} \approx 4.4 \Rightarrow x \approx 460 \text{ s}$$

$$\frac{670}{y} = 4.4 \Rightarrow y \approx 150 \text{ mmHg}$$

33.(B) Rate law for the given reaction,

$$\text{Rate} = -\frac{1}{3} \frac{d[A]}{dt} = +\frac{1}{2} \frac{d[B]}{dt}$$

34.(B) We know

$$\Delta_r H = (E_a)_{\text{forward}} - (E_a)_{\text{reverse}}$$

$$\Rightarrow (E_a)_{\text{reverse}} = (E_a)_{\text{forward}} - \Delta_r H = 77 - 72 = +5 \text{ kJ mol}^{-1}$$

35.(A) We know that

$$\text{Activity} \left(-\frac{dN}{dt} \right) \propto N$$

$$N = N_0 \left(\frac{1}{2}\right)^n \Rightarrow \frac{N}{N_0} = \left(\frac{1}{2}\right)^n \Rightarrow \frac{1}{10} = \left(\frac{1}{2}\right)^n \Rightarrow 10 = 2^n$$

Taking log on both the sides, $\log 10 = n \log 2$

$$n = \frac{1}{0.301} = 3.32 \text{ (as } \log 2 = 0.3010\text{)}$$

Therefore, $t = n \times t_{1/2} = 3.32 \times 30 = 96.6$ days

36.(A) The time taken for completion of the whole reaction is

$$t = \frac{2.303}{k} \log \left(\frac{a_0}{a_0 - x} \right)$$

For 40% completion of the reaction, $t_1 = \frac{2.303}{k} \log \left(\frac{10}{6} \right) = 1$ h

If the initial concentration, that is, $a = 5 \text{ mol L}^{-1}$, then

$$t_2 = \frac{2.303}{k} \log \left(\frac{5}{5-x} \right)$$

Given that $t_1 = t_2 = 1$ h. So,

$$\log \left(\frac{5}{3} \right) = \log \left(\frac{5}{5-x} \right)$$

or

$$\frac{5}{3} = \frac{5}{5-x} \text{ or } x = 2$$

Therefore, the percentage of reaction completed is $\frac{2}{5} \times 100 = 40\%$

37.(B) For the reaction $\frac{1}{2}A \rightarrow 2B$ for instantaneous rates,

$$\begin{aligned} \frac{dx}{dt} &= \frac{-2d[A]}{dt} = + \frac{d[B]}{2dt} \\ \Rightarrow \frac{1}{2} \frac{dx}{dt} &= \frac{-d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt} \end{aligned}$$

38.(D) We know

$$k = \frac{[R]_0 - [R]_t}{t}$$

$$\Rightarrow 2 \times 10^{-2} = \frac{[R]_0 - 0.5}{25}$$

$$\Rightarrow [R]_0 = 50 \times 10^{-2} + 0.5 = 1.0 \text{ M}$$

39.(D) $(\text{Rate})_{\text{initial}} = k (n/V) \times (n/V)$

$(\text{Rate})_{\text{final}} = k (4n/V) \times (4n/V)$

So,
$$\frac{(\text{Rate})_{\text{initial}}}{(\text{Rate})_{\text{final}}} = \frac{16}{1}$$

40.(C) The rate of reaction increases on increasing the temperature due to greater number of molecules having average energy.

41.(C) From the given rate law, the order of the reaction is
 Order = $1/2 + 1/4 + 0 = 3/4$.

42.(B) For the first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10} = 0.0693$$

So,
$$t = \frac{2.303}{0.0693} \log \frac{0.08}{0.01} = 30 \text{ min}$$

43.(A) Rate = $k[A]^1 \Rightarrow \text{M s}^{-1} = k[M]^1 \Rightarrow k = \text{s}^{-1}$
 Rate = $k[A]^0 \Rightarrow \text{M s}^{-1} = k$

44.(C) For first order reaction, $t_{1/2}$ is independent of the concentration of reactant.

45.(B) For a first order reaction

$$t_{0.5} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{t_{0.5}}$$

When the reaction is 75 % complete,

$$t_{0.75} = \frac{2.303}{k} \log \frac{[a]}{[a-x]} = \frac{2.303}{k} \log \frac{[a]}{[a-0.75a]}$$

$$t_{0.75} = \frac{2.303}{k} \log 4 = \frac{2.303}{0.693} \times t_{0.5} \times 0.603 = 2t_{0.5}$$

46.(B) $k = Ae^{-E_a/RT} \Rightarrow A = \ln k + \frac{E_a}{RT} \Rightarrow \text{Units of } A = \text{s}^{-1} + \frac{\text{J mol}^{-1}}{\text{J K}^{-1} \text{mol}^{-1} \times \text{K}} = \text{s}^{-1}$

47.(B) Given that $t_{1/2} = 5730 \text{ y}$. If a is the initial ^{14}C activity in a living tree, then

Activity in the dead wood, $a_t = \frac{80}{100} \times a$

The nuclear/radioactive decays follow the first-order kinetics. So,

$$t = \frac{2.303}{k} \log \frac{a}{a_t} \text{ and } k = \frac{0.693}{t_{1/2}}$$

Therefore,
$$t = \frac{2.303}{0.693/t_{1/2}} \log \frac{a}{\frac{80}{100}a} = \frac{2.303 \times 5730 \text{ y}}{0.693} \log \frac{100}{80} = 1845.4 \text{ y}$$

48.(C) We know

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

$$\Rightarrow \frac{dk}{k} = \frac{E_a}{RT^2} dT$$

Given that $\frac{dk}{k} = \frac{11.11}{100}$; $dT = 1^\circ\text{C}$; $T = 27^\circ\text{C} = 300 \text{ K}$

Therefore,
$$0.111 = \frac{E_a \times 1}{1.987 \times 300 \times 300} \Rightarrow E_a = 0.1111 \times 1.987 \times [300]^2$$

At 127°C ,
$$\frac{dk}{k} = \frac{E_a}{1.987 \times (400)^2} = \frac{0.111 \times 1.987 \times (300)^2}{1.987 \times (400)^2} = 0.1110 \times \left(\frac{3}{4}\right)^2 = 0.06249$$

Hence, the percentage increase is 6.25%.

49.(D) According to the Arrhenius equation

$$\log k = \log A - \frac{E_a}{2.303RT}$$

Given that $\frac{E_a}{2.303R} = S \Rightarrow E_a = 2.303RS$.

50.(A) Extent of reaction = 30% and time taken = 40 min

For a first-order reaction,

$$t = \frac{2.303}{k} \log \frac{a}{a-x} = \frac{2.303}{k} \log \frac{1}{1-(x/a)}$$

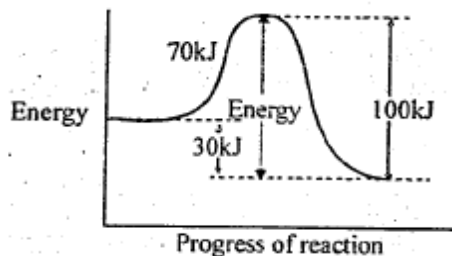
$$40 \text{ min} = \frac{2.303}{k} \log \left(\frac{1}{1-0.3} \right)$$

or
$$k = \frac{2.303}{40 \text{ min}} \log \frac{1}{0.7} = 8.92 \times 10^{-3} \text{ min}^{-1}$$

We know, for a first-order reaction, $t_{1/2} = \frac{2.303 \log 2}{k}$

Then,
$$t_{1/2} = \frac{2.303 \log 2}{8.92 \times 10^{-3} \text{ min}^{-1}} = 77.7 \text{ min}$$

51.(D) $\Delta H = E_{af} - E_{ab} \Rightarrow E_{ab} = E_{af} - \Delta H = 70 - (-30) = 100 \text{ kJ mol}^{-1}$



52.(B) As reaction given in option (B) is involves single reactant only.

53.(B) Given that $k_{10} = k_{283} = 4.5 \times 10^3 \text{ s}^{-1}$, $k_T = 1.5 \times 10^4 \text{ s}^{-1}$, $T = ?$.

Also $E_a = 60 \text{ kJ mol}^{-1} = 60000 \text{ J mol}^{-1}$. Using Arrhenius equation, one can write

$$\log \frac{k_T}{k_{283}} = \frac{E_a}{2.303 R} \left[\frac{1}{283} - \frac{1}{T} \right]$$
$$\log \frac{1.5 \times 10^4 \text{ s}^{-1}}{4.5 \times 10^3 \text{ s}^{-1}} = \frac{6000 \text{ J mol}^{-1}}{2.303 \times 8.3 \text{ J K}^{-1} \text{ mol}^{-1}} \left[\frac{T - 283}{283 \times T} \right]$$

On solving, we get $T = 297 \text{ K} = 24^\circ\text{C}$.

54.(A) More is the temperature coefficient, more is the activation energy.

55.(A) Rate of reaction $= -\frac{\Delta[\text{O}_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{SO}_3]}{\Delta t}$

Therefore, rate of disappearance of O_2 is related to rate of formation of SO_3 as

$$-\frac{\Delta[\text{O}_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{SO}_3]}{\Delta t}$$

<H2> Multiple Correct Choice Type

1.(A, B, D) For the given first-order reaction, the rate equation is

$$\frac{-d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$$

The concentration of the reactant at any time t is given by

$$t = \left(\frac{2.303}{k} \right) \log \frac{a}{a-x}$$

where $a = 100$ and $a - x = 100 - 99.6 = 0.4$. Hence, concentration of N_2O_5 decreases exponentially with time.

Half-life period for first-order reaction

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

It is independent of the concentration of the reactant. We know that k increases with increase in temperature (according to Arrhenius equation) and since $t_{1/2}$ is inversely proportional to k , so $t_{1/2}$ decreases, when k increases with increase in temperature.

When the reaction is 99.6% complete, then

$$t_{99.6} = \left(\frac{2.303}{k} \right) \log \frac{100}{0.4}$$
$$t_{99.6} = \left(\frac{2.303}{k} \right) 2.4 = 8 \times \frac{0.693}{k} = 8t_{1/2}$$

2.(A, B, D)

Option (A): We know the relation,

$$\log K_p = -\frac{\Delta_r H}{R} \times \frac{1}{T} + \frac{\Delta_r S}{R}$$

A plot of $\log K_p$ vs. $1/T$ is linear.

Option (B): For first order reaction, $X \rightarrow P$.

$$k = \frac{2.303}{t} \log \left(\frac{P}{X} \right)$$

A plot of $\log [X]$ vs. time is linear.

Option (C): At constant volume,

$$\frac{P}{T} = \text{Constant.}$$

Option (D): At constant temperature,

$$pV = \text{Constant.}$$

3.(B, C) $\text{RCI} + \text{NaOH} \rightarrow \text{ROH} + \text{NaCl}$

The rate expression is $\text{Rate} = k[\text{RCI}]$. So, rate of reaction is unaffected by doubling positive concentration of NaOH, because it does not import in rate law equation. The rate of reaction is increased by increase in temperature.

4.(A, B, C) Concept based.

5.(A, B) Given that $100 \propto (0.1)^{1-n}$ and $50 \propto (0.025)^{1-n}$.

Dividing, we get $2 = 4^{1-n}$

$$\text{or } \log 2 = (1-n) \log 4 \text{ or } 1-n = \frac{\log 2}{\log 4}$$

$$\text{or } n = 1 - \frac{\log 2}{\log 4} = 1 - \frac{\log 2}{2 \log 2} = 1 - \frac{1}{2} = \frac{1}{2}$$

We have $100 \propto (0.1)^{1/2}$ and $t_{1/2} \propto (1)^{1/2}$. Dividing these two, we get

$$\frac{t_{1/2}}{100} = \left(\frac{1}{0.1} \right)^{1/2} \text{ or } t_{1/2} = 100\sqrt{10} \text{ min}$$

6.(A, B, D) We know

$$k = \frac{2.303}{t} \log \left(\frac{\text{Product}}{\text{Reactant}} \right) \quad (1)$$

Substituting the values in Eq. (1), we get

$$k = \frac{2.303}{30} \log \frac{30 - (-15)}{20 - (-15)}$$

$$\Rightarrow k = \frac{2.303}{30} \log \frac{45}{35} = 8.38 \times 10^{-3} \text{ min}^{-1}$$

For the half life of first order reaction, we have

$$t_{1/2} = \frac{0.693}{k}$$

$$\Rightarrow t_{1/2} = 82.17 \text{ min.}$$

Again, substituting the values in Eq. (1), we get

$$t = \frac{2.303}{0.00838} \log \frac{45}{0 - (-15)}$$

$$\Rightarrow t = 131.13 \text{ min}$$

At half time

$$\frac{30 - (-15)}{x - (-15)} = 2$$

$$\Rightarrow \frac{45}{x + 15} = 2$$

$$\Rightarrow x + 15 = \frac{45}{2}$$

$$\Rightarrow x = 22.5 - 15 = 7.5^\circ$$

7.(A, D) Rate of reaction $\propto \frac{1}{E_a}$

Catalyst increases rate of reaction, so, activation energy decreases.

Catalyst also alters positive rate of reaction.

$$8.(A, B) \text{ Percentage of cyclohexane} = \frac{k_1 \times 100}{k_1 + k_2} = \frac{1.26 \times 10^{-4}}{1.26 \times 10^{-4} + 3.8 \times 10^{-5}} \times 100 = 77\%$$

Therefore, percentage of methylcyclopentane = 23%.

9.(A, C) For the reaction $4\text{NH}_3(\text{g}) + \text{SO}_2 \rightarrow 4\text{NO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$,

$$\begin{aligned} -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} &= -\frac{1}{5} \frac{d[\text{O}_2]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt} \\ -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} &= -\frac{1}{5} \frac{d[\text{O}_2]}{dt} \text{ or } -\frac{d[\text{NH}_3]}{dt} = -\frac{4}{5} \frac{d[\text{O}_2]}{dt} \text{ or } -\frac{d[\text{NH}_3]}{dt} = \frac{d[\text{NO}]}{dt} \end{aligned}$$

10.(A, B, C)

(A) $t_{x\%} \propto \frac{1}{a}$ for second order

(B) Rate = $kC_1 = kC_0 e^{-kt}$

$$\ln\left(\frac{dc}{dt}\right) = \ln(\text{rate}) = \ln k C_0 - kt$$

Hence, a straight line is observed.

$$(C) k = Ae^{-E_a/RT}$$

$$\text{Rate} = k(\text{conc.})^n = Ae^{-E_a/RT} (\text{conc.})^n$$

$$\ln(\text{rate}) = -\frac{E_a}{RT} + \text{constant}$$

Therefore, the slope is $-E_a/R$.

$$(D) \frac{t_{0.75}}{t_{0.5}} = \text{ratio of time is constant with initial concentration.}$$

11.(A, B, C, D) Slow step is rate determining step, from slow step $-\frac{d}{dt}[\text{O}_3] = k[\text{O}_3][\text{O}]$

Molecularity for Step 1 is 1 and for Step 2 is 2 as shown in above given reaction.

12.(A, B) The rate expressions are as follows:

$$(A) \text{Rate}_A = k[3\text{NO}_2][3\text{I}^-][3\text{H}^+]^2 = 81(\text{Rate})$$

$$(B) \text{Rate}_B = k[2\text{NO}_2][(1/2)\text{I}^-][2\text{H}^+]^2 = 4(\text{Rate})$$

$$(C) \text{Rate}_C = k[2\text{NO}_2][2\text{I}^-][\text{H}^+]^2 = 4(\text{Rate})$$

$$(D) \text{Rate}_D = k[\text{NO}_2][\text{I}^-][3\text{H}^+]^2 = 9(\text{Rate})$$

13.(A, C) We know

$$t_{1/2} \propto \frac{1}{P^{n-1}}$$

$$\Rightarrow \frac{21}{11} = \left(\frac{48}{92}\right)^{n-1}$$

$$\Rightarrow n = 0$$

Therefore, for the zero order,

$$t_{1/2} = \frac{P}{2k}$$

$$\Rightarrow k = \frac{P}{2t_{1/2}} = \frac{11}{2 \times 48} = 0.114\text{s}^{-1}$$

<H2> Assertion–Reasoning Type

1.(A) Pseudo unimolecular reaction is the reaction whose order is one and molecularity is two. So in this reaction, at least two reactants are present.

2.(A) Molecularity of a reaction cannot be determined experimentally because molecularity is assigned to the reactions on the basis of mechanism.

3.(B) Order is the sum of power of concentration terms which change with time, but molecularity is the sum of stoichiometric coefficients of a balanced equation of reaction.

4.(B) Rate of reaction $\propto \frac{1}{\text{Activation energy}}$

A catalyst decreases the potential energy, due to which rate of reaction increases.

5.(B) For a first order reaction,

$$[A]_f = [A]_0 \exp(-kt)$$

$$[A]_0 - [A]_f = [A]_0 - [A]_0 \exp(-kt) = [A]_0 (1 - \exp(-kt))$$

or

$$\frac{[A]_0 - [A]_f}{[A]_0} = (1 - \exp(-kt))$$

So, degree of dissociation = $(1 - \exp(-kt))$

For a first order reaction,

$$k = A \exp(-E_a / RT) = A \exp\left(\frac{\text{J mol}^{-1}}{\text{J mol}^{-1} \text{K}^{-1} \text{K}}\right)$$

Thus, the units of A are the same as that for k. For a first-order reaction, the units of k are those of time⁻¹. So the units of A are also those of time⁻¹.

6.(B) The reaction, $\text{N}_2(10 \text{ atm}) + 3\text{H}_2(10 \text{ atm}) \rightarrow 2\text{NH}_3(\text{g})$ is faster because of higher partial pressures of the reactants.

7.(B) The expression is $\ln \frac{a}{a-x} = kt$ or $\frac{a}{a-x} = e^{-kt}$

8.(C) For second order, $k = \frac{1}{t} \frac{x}{a(a-x)}$. This is of the form $y = mx + c$ and is a straight line.

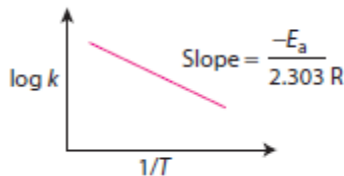
9.(B) Concept based. Both statements individually are correct.

<H2>Comprehension Type

1.(B) The equation is $\log k = \log A - E_a/RT$ where k for second-order reaction has the units $\text{L mol}^{-1} \text{s}^{-1}$; E_a is in J; R is in $\text{J K}^{-1} \text{mol}^{-1}$; and T is in K. So, we get units of A as $\text{L mol}^{-1} \text{s}^{-1}$.

2.(C) According to Arrhenius equation, $\log k = -E_a/2.303RT + \log A$

Comparing it with straight line equation $y = mx + c$, we get slope as $-E_a/2.303R$ on plotting $\log k$ vs. $1/T$ as shown:



3.(C) We know

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Given, $E_a = 87 \times 10^3 \text{ J mol}^{-1}$, we get

$$T_2 = 37^\circ\text{C} = 37 + 273 = 310 \text{ K}$$

$$T_1 = 15^\circ\text{C} = 15 + 273 = 288 \text{ K}$$

Substituting the values in Eq. (1), we get

$$\log \frac{k_2}{k_1} = \frac{87000}{2.303 \times 8.314} \left(\frac{310 - 288}{310 \times 288} \right)$$

$$\log \frac{k_2}{k_1} = 1.11$$

$$\Rightarrow \frac{k_2}{k_1} = \text{antilog}(1.11) = 12.88 \approx 13/1$$

4.(B) The expression is $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

where $k_2/k_1 = 2$, $T_1 = 298 \text{ K}$ and $T_2 = 308 \text{ K}$.

Substituting the values, we get

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \left(\frac{308 - 298}{308 \times 298} \right)$$

$$\text{Therefore, } E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 308 \times 298}{10} = 52897.77 \text{ J mol}^{-1} \text{ or } 52.89 \text{ kJ mol}^{-1}$$

5.(B) This is because according to Arrhenius, the fraction of molecules is given by $e^{E_a/RT}$.

Let $x = e^{E_a/RT}$ Taking ln on both the sides, we get

$$\ln x = -\frac{E_a}{RT}$$

6.(A) Since the reaction is of zero order with respect to B, hence any change in the concentration of B has no effect on the rate of reaction.

From experiment I, $2.0 \times 10^{-2} \text{ M min}^{-1} = k \times (0.1)^1$

$$\text{So, } k = \frac{2.0 \times 10^{-2} \text{ M min}^{-1}}{0.1 \text{ M}} = 0.2 \text{ min}^{-1}$$

For experiment II,

$$4.0 \times 10^{-2} \text{ M min}^{-1} = 0.2 \text{ min}^{-1} [\text{A}]$$

$$[\text{A}] = \frac{4.0 \times 10^{-2} \text{ M min}^{-1}}{0.2 \text{ min}^{-1}} = 0.2 \text{ M}$$

7.(B) For experiment III, Rate = $0.2 \text{ min}^{-1} \times (0.4 \text{ M})^1 = 0.08 \text{ M min}^{-1}$

8.(C) For experiment IV, $2.0 \times 10^{-2} \text{ M min}^{-1} = 0.2 \text{ min}^{-1} \times [\text{A}]$

or
$$[\text{A}] = \frac{2.0 \times 10^{-2} \text{ M min}^{-1}}{0.2 \text{ min}^{-1}} = 0.1 \text{ M}$$

<H2> Integer Answer Type

1.(4) In general, $t_{1/2} \propto \frac{1}{[\text{A}]_0^{n-1}}$. Given that $t_{1/2} \propto \frac{1}{[\text{A}]_0^3}$, this means $n - 1 = 3$ or $n = 4$.

2.(8) We know that $k = \frac{2.303}{t} \log \left[\frac{a}{a-x} \right]$

Substituting given values, we get

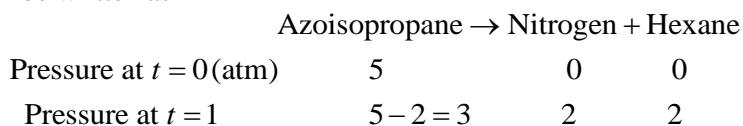
$$k = \frac{2.303}{24} \log \left[\frac{1}{0.125} \right] \text{ or } k = 0.0867 \text{ h}^{-1}$$

Therefore, $t_{1/2} = 0.693/k = 7.99 \text{ h} \approx 8 \text{ h}$.

3.(2) Looking at the units of rate constant we can say that the reaction is of second order. In general, Units of $k = (\text{time})^{-1} \times (\text{conc.})^{n-1}$.

4.(4) The order of the reaction is one, it is a pseudo unimolecular reaction in which one of the reactant, that is, H_2O is taken in excess.

5.(7) The reaction can be written as



Total pressure exerted by mixture at this time = $3 + 2 + 2 = 7 \text{ atm}$.

6.(3) The reaction is $2\text{A} \rightarrow \text{A}_2$. The expression for rate of reaction is Rate = $k[\text{A}]$.

$$\text{Rate} = k[\text{X}]^a \quad (1)$$

$$27(\text{Rate}) = k[3X]^a \quad (2)$$

Dividing Eq. (1) by Eq.(2), we get

$$\frac{1}{27} = \left[\frac{1}{3} \right]^a$$

So, $a = 3$ or order = 3.

<H2> Matrix–Match Type

1.(A) → (r); (B) → (p); (C) → (r); (D) → (q)

Molecularity is the number of reactants take part in an react.

2.(A) → (q); (B) → (p); (C) → (s); (D) → (r)

Concept based.

3.(A) → (r); (B) → (q); (C) → (p); (D) → (s)

(A) → (r): Half-life of first order reaction $(t_{1/2}) = \frac{0.693}{k}$

(B) → (q): Arrhenius equation is

$$k = Ae^{-E_a/RT}$$

(C) → (p): Molar concentration is active mass that take part in a reaction.

(D) → (s): Half-life period of zero order reaction $(t_{1/2}) = \frac{a}{2k}$

4.(A) → (q); (B) → (r); (C) → (t); (D) → (u)

$$(A) \quad 2.303 \log_{10} \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

Putting $T_2 = 298$ K; $T_1 = 273$ K, $E_a = 65,000$ J, $R = 8.314$ J (mol K), we get

$$\frac{k_2}{k_1} = 11$$

(B) $\frac{2.5}{20} = \frac{1}{8} = \left(\frac{1}{2} \right)^n$ or $n = 3$ or $t = 3 \times \frac{0.693}{0.0693} = 30$

(C) Zero order: $t_{1/2} = \frac{a}{2K}$, For first order: $t_{1/2} = \frac{0.693}{K}$

$$\frac{1}{2k_1} = \frac{0.693}{k_2} \text{ or } \frac{k_2}{k_1} = 2 \times 0.693$$

(D) $t_{1/2} \propto (a)^{1-n}$ or $(1-n) = \frac{\log t'_{1/2} - \log t''_{1/2}}{\log a' - \log a''}$

$$t_{1/2} \propto \frac{1}{a^{n-1}} \text{ or } \frac{480}{240} = \left(\frac{0.0677}{0.136} \right)^{n-1}$$

or $n = 0$

